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Preferential Flow Pathways and Their Capacity to Transport Isoproturon in a Structured Clay Soil

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Abstract: A field experiment was established to monitor preferential flow pathways and their capacity to transport isoproturon in a heavy clay soil. A hydrologically defined plot of 600 m^2 at a field site on the Oxford University Farm at Wytham was created with integral flow monitoring and sampling devices. Data are presented from two flow events which occurred in April and May 1994. The highest concentrations of isoproturon (130 μg litre^{-1}) were observed in the drainage system. The vast majority of the 0·7% of applied pesticide that left the plot was *via* the drainage system (75–90%) with lateral subsurface flow accounting for a smaller proportion (max 23%). Whilst high pesticide concentrations could be found in overland-flow water, the volumes of water moved by this route were small (max 3%). Less water was estimated to have left the field in response to rainfall than in the previous year. This was attributed to decay of the mole drain system. Consequently the amount of applied pesticide lost in runoff (0·7%) was less than that estimated for the first year (1·5%). The work has shown that, even when a farmer follows best practice in the application of a herbicide to a winter cereal in a drained clay field, high concentrations of the herbicide (relative to the EC drinking water limit) will contaminate surrounding watercourses.

Key words: isoproturon, bypass flow, drain flow, subsurface lateral flow, overland flow

1 INTRODUCTION

The phenomenon of preferential or bypass flow of water in structured soils is receiving increasing attention from scientists,[1–3] agrochemical companies and regulatory bodies.[4] During bypass flow, high concentrations of chemicals can be transported from the field to nearby watercourses.[5–7] Clearly, this is an important issue from the environmental standpoint, as this flow mechanism can lead to rapid contamination of surrounding water courses and possibly of groundwater.

Estimates of the total loss of pesticides to surfce water as a proportion of that applied indicate that no more than 1% is usually lost in this manner. However, this loss may be concentrated into just a few events in which the concentration of pesticides in the receiving watercourses may be three orders of magnitude greater than the EC limit for drinking water of 0·1 μg litre^{-1}.[8] Whilst there is not yet a great deal of evidence available, temporary peaks of herbicide or insecticide may lead to deleterious effects on the local flora and fauna.[9,10]

Soils that exhibit preferential water flow behaviour in England and Wales generally have a high clay content. The small pore diameter of the clay soil matrix permits only very slow water ingress. In winter, the topsoil soon becomes saturated under normal rainfall conditions.[11] To make farming, and in particular the growing of winter cereals, viable on these soils, the installation of a drainage system is recommended.[12] Thus, macropores both natural (e.g. worm channels) and artificial (left by the moling process) feed excess rainwater into the drainage system, thereby alleviating the waterlogging problem.[5]

This study has used isoproturon, a herbicide widely used in the UK to control blackgrass in winter cereals. Isoproturon has been identified as a major contributor

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to contraventions of standards in water-supply zones in the Thames region.[4] The field site at Wytham is on a heavy clay soil of the Denchworth series, with an extensive drainage system (including mole drains). The field has a winter cereals/oilseed rape rotation. The first field season studied soil hydrology, and also the transport of isoproturon, but in a largely qualitative manner. The work indicated that in response to rain storms in late winter and early spring, water moved rapidly both over the soil (overland flow) and through it to the drainage system. Some evidence also indicated that water moved laterally through the topsoil by bypass flow (lateral subsurface flow). High pesticide concentrations were found in water collected during these events (up to 500 μg litre^{-1} in the drain water).[6] Information from the soil hydrological instruments indicated that preferential flow either laterally or vertically was preceded by the onset of saturation and the development of a temporary perched water table in the topsoil.[13] No rise in the water table to the height of the drains was noted during any of the preferential flow events.

To follow the first-year study, an attempt was made to quantify the water movement and the pesticide load in the different preferential pathways in order to ascertain their relative importance. To achieve this, a 600 m^2 section of the field was hydrologically isolated using ditches and the existing drainage system. The experiment was therefore designed to assess the importance of, and differentiate between, overland flow, lateral subsurface flow and drain flow.

2 MATERIALS AND METHODS

2.1 Location and description

The field site was located on the Oxford University Farm at Wytham in Oxfordshire. The field is currently in winter-cereal cultivation. In this regime, three years of winter cereals is normally followed by one season of oilseed rape. The 1993/4 season described in this paper represented the third successive year of winter-cereal production in this field. The field slopes by 2–5° down to a drainage ditch. The ditch is protected by a 3-m uncultivated buffer strip. The field is drained by plastic, slotted drains 80 cm below the soil surface, backfilled with aggregate to 45 cm from the surface. These empty into the ditch at 30-m intervals. Lateral mole drains are present 50 cm below the soil surface at 3-m intervals. They run through (and drain into) the aggregate above the plastic drains. Mole drains were installed in August 1992.

The experimental plot was located in the midslope of the field, about 80 m upslope of the ditch, in an area of soil classified as Denchworth Series. Particle analysis of the soil gave a clay content of around 57% in the Ap horizon (0–26 cm) and 63% in the Bg horizon (26–54 cm). The percentage of organic carbon ranged from 3·1 in the Ap horizon to 0·9 in the Bg horizon.

2.2 Isolation of the plot

In order to measure both water movement and pesticide loss *via* different flow routes, a portion of the field was hydrologically isolated. The selected plot area was of a homogeneous soil type. After the previous winter wheat crop had been harvested in August, a 600 m^2 plot was isolated from the rest of the field. The site slopes down from North to South, leading to a ditch at the bottom of the field. In addition, the field slopes gently from East to West. The aim was to prevent lateral water movement into the plot, and to prevent it escaping from the plot, other than *via* waterflow-measuring devices. Field drain 2 on the west side of the plot collects water from the mole drains to the east of its position, and thus formed the western boundary of the plot. Above mole 33 the field drain was truncated, so that it could no longer collect water from higher up the field (Fig. 1). At the bottom of the plot, after mole 22, the field drain was cut and the end fed into a plastic collecting pipe. The field drain truncated above the plot was connected to an 82-mm pipe and brought round the plot at a depth of 80 cm. It was then re-connected to the original field drain at the bottom of the plot. In this way the plot could operate as a separate hydrological unit without disturbing the overall field drainage. At the eastern side of the plot, 20 m from the field drain, a ditch was dug to a depth of 60 cm. The purpose of this ditch was to truncate the moles, thereby preventing lateral flow into the field drain from any point to the east of it. At the northern, uppermost point of the plot, a ditch was dug down to 50 cm and corrugated plastic sheeting was installed and bedded into the dense Bg horizon, so that the sheeting was proud of the soil surface when the ditch was back-filled. This was to prevent lateral subsurface flow or overland flow, from entering the plot.

At the southern or bottom end of the plot, two lateral-flow collectors were constructed. One was positioned below ground to collect lateral subsurface flow, and another was prepared on the soil surface to collect overland flow. These are described in greater detail below.

2.3 Soil and water-flow measuring and sampling

For the purpose of this experiment, overland flow is considered to comprise water that is moving laterally between 0 and 5 cm; lateral subsurface flow is that running laterally between 5 and 30 cm; and drain flow is water in the field drain collected by the mole drains on the plot. Outflows from the isolated plot were mea-

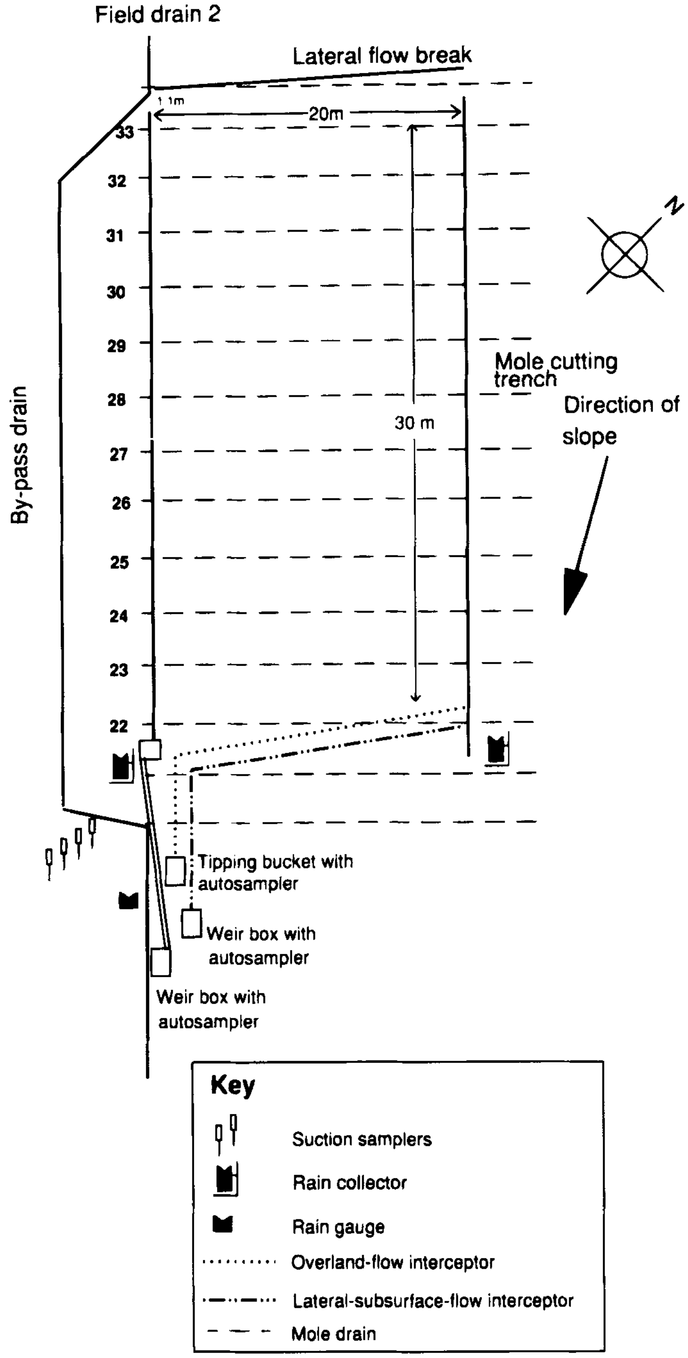

Fig. 1. Location of water-monitoring and sampling devices at Wytham (superimposed over field and mole drains).

sured to establish the importance of the various flow pathways within the water balance. A schematic diagram illustrating the sampling devices is shown in Fig. 2.

2.3.1 Soil sampling

To assess the persistence of the herbicide in the field, 1 kg of soil was collected from the upper 2 cm of the soil surface with a spatula. Soil from this shallow depth was believed to be the most relevant in representing the majority of pesticide available for pick-up in a storm/preferential flow event. In a rain storm/preferential flow situation, once the infiltration capacity of the soil matrix is exceeded, the new rainwater will skim over the surface, picking up pesticide prior to moving down a macropore and by-passing much of the deeper soil matrix.[13] Starting 12 days after spraying, soil sampling was done on a weekly basis. The soil was collected from 1-m^2 plots, which were sampled in sequence from one end of the experimental plot to the other. At the end of the season (July) an attempt was made to assess whether pesticide residues had penetrated below the topsoil. This was done by digging a small shallow trench, and

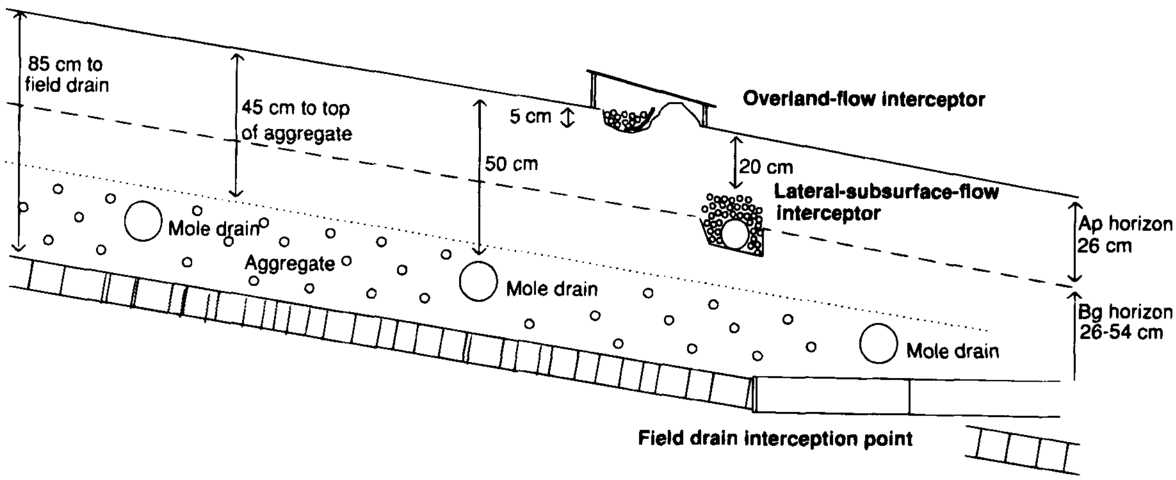

Fig. 2. Schematic diagram of preferential-flow capturing devices at the bottom of the plot.

using a spade and trowel to remove sequentially soil of increasing depths from the side of the trench. The soil was bagged and frozen prior to analysis for isoproturon.

2.3.2 *Sampling rainwater*

Two sets of collectors (20 m apart) were installed at either end of the plot, each set comprising three collectors. The collectors took the form of a 15-cm diameter funnel over a 1-litre plastic bottle, held in an assembly 30 cm above the soil surface. A gauze mesh was held in place in the funnel to prevent large particulates or insects entering the sampling bottle. No sorption of [^{14}C]isoproturon to the plastic bottles used for collecting rainwater was found when tested.

2.3.3 *Sampling overland flow water*

With the completion of cultivation, an overhand-flow interceptor was created over the position of the lateral-flow interceptor by forming a 5-cm gully by hand, which was smeared and filled with gravel. The downslope 'wall' of the gully was protected with a 20-cm band of impermeable butyl rubber, which was buttressed with soil. The end of the gully led into an 82-mm diameter pipe, which conveyed water 15 m downslope to a measuring point, as with the other flow-measuring devices. Clay was smeared around the entrance of the pipe to ensure that the water moving down the gully would enter it. This clay-smeared connection was kept moist over the sampling period to ensure that it did not crack. The measuring device, a 1-litre tipping-bucket apparatus, was installed in a 1 × 0·5 m plastic tank. The number of tips in a 10-min interval was logged. The tank collected all the water once it had passed through the tipping bucket, and it was then fed *via* a short pipe to a 160-mm diameter sampling pot, which could accommodate 1·5 litre of water. Once the pot filled, a float switch would trigger an autosampler (Dalog Sampling Equipment, Alton, UK) to take a single 1-litre sample. This cycle could be repeated until the autosampler had taken all of its 24 possible samples.

2.3.4 *Sampling soil-macropore water*

Suction samplers were installed at two depths (0·25 and 0·5 m) close to the isolated plot. Holes were first augered down to the appropriate depth, before the suction sampler was bedded into silica flour at the bottom of the hole. The space between the suction-sampler tube and the soil was filled with powdered bentonite. Over the course of a few weeks the bentonite swelled, having adsorbed water from the surrounding soil and from rainfall events, which sealed the suction samplers into their holes. Prior to spraying, the tube exposed at the soil surface was covered and capped to prevent any spray droplets from touching the assembly.

Sampling was done by generating a vacuum with a handpump to achieve 0·5–0·7 bar, and by collecting the soil water over a 15-min period. This suction was only sufficient to empty the surrounding macropores, as opposed to the smaller pores in the soil matrix. No more than 100 ml was collected per suction sampler in this manner.

2.3.5 *Sampling lateral subsurface water*

At the bottom of the plot, a ditch was dug down to 40 cm and linked to an 82-mm diameter pipe. The junction was sealed with puddled clay, and the pipe was led down to a measuring point 15 m downslope. The ditch was then back-filled with slotted drain pipe and gravel, to a depth of 24 cm, and then packed with soil to the soil surface. The flow-measuring device comprised of a V-notch weir in which a pressure transducer determined the height of water within the weir, and the use of calibration equations enabled a flow rate to be deduced. The weir box also contained a float switch and Teflon sampling tube. The float switch was set at a height in the weir box equivalent to a flow of 0·02 litre s^{-1}; when triggered, the autosampler would take 24 × 1-litre samples at 30-min intervals in sequence.

2.3.6 Sampling field-drain water

The join between the plastic slotted field drain and the 82-mm interception pipe was effected by packing with puddled clay. As with the other collecting devices, the plastic pipe was fed down field so that a slope could be maintained, but the water could be brought to a measuring point at the surface (some 15 m downslope from the point of interception). The V-notch weir and sampling device was identical to that used for lateral subsurface flow measurement and sampling. In this case the float switch was set to trigger the autosampler to take its 24 × 1-litre samples at 30-min intervals when the level in the weir box was equivalent to 0·05 litre s^{-1}.

2.4 Field procedure on spraying day

Immediately prior to application of the herbicide, care was taken to prevent contamination of the water samplers with the spray. The rain collectors were taken off and the automatic water samplers were protected with plastic sheeting. Five sets of four Whatman no. 1 filter papers each 10 cm in diameter were pinned to wooden battens and placed across the plot to measure the pesticide application in the spray. When the spraying had been completed, the filter papers were placed in plastic bags and stored in a freezer. They were assessed for isoproturon by extraction in methanol prior to high-performance liquid chromatography (HPLC) analysis. In addition, soil samples were taken from three points near the plot for soil residue analysis, and processed in the same way as the filter papers.

2.5 Sample collection, preparation, concentration and analysis

Once the installation was complete, soil, rainwater and macropore water were collected manually on a weekly basis. The other samples were taken automatically. Additional samples were taken as necessary following storm events. Water samples were maintained at 4°C for up to one month prior to analysis. When, on occasion, the concentration of isoproturon in samples was double-checked, and further samples taken from the original bottle, no change greater than 10 μg litre^{-1} from the original figure was found after further storage of up to one month. In most cases analysis was completed within a week of the receipt of field samples. Prior to isoproturon analysis, where concentrations were believed to be low, samples were first concentrated using C18 bond elute cartridges (Sorbex) and eluted from the cartridges with 2 ml methanol. Samples were taken into the HPLC *via* a 150-μl loop. A C18 column Supelcosil™ LC-ABZ (Supelco UK, a branch of Aldrich-Sigma Ltd) was used (4·6 mm × 25 cm) with acetonitrile + water (35 + 65 by volume) as eluent. Detection was made at 240 nm, and peak purity was checked by comparing the absorbance at 220 nm. The detection limit was 10 μg litre^{-1}. Soil samples were analysed for isoproturon by taking four 50-g samples and extracting with 100 ml methanol prior to determination by HPLC. [^{14}C]isoproturon was used to spike 2-mm air-dried soil to test the efficiency of this extraction technique. The recovery of the radiolabelled isoproturon varied between 87 and 100%.

Prior to chloride, sulfate and nitrate analysis, a 10-ml aliquot was taken from the original water sample and filtered using 0·45-μm disposable filters (Millipore) into 30-ml disposable bottles (Sterilin). The 0·45-μm filter would remove the majority of bacteria from the sample, and so prevent isoproturon loss by assimilation by bacteria during storage (up to one month at 4°C). Samples were analysed using a Dionex ion chromatograph. The eluent used contained 1·8 mM sodium bicarbonate and 1·7 mM sodium carbonate. The regenerant used was 25 mM sulfuric acid. Detection was by electrical conductivity.

3 RESULTS AND DISCUSSION

3.1 Isoproturon found in water samples prior to spraying

On a number of occasions, isoproturon was detected (0·27–0·53 μg litre^{-1}) during November 1993 in the rainwater collectors on the plot prior to spraying. Low concentrations of isoproturon (1·6 μg litre^{-1}) were also detected in overland-flow water, even as long as 331 days after it had last been applied to the field. This was notwithstanding the ploughing and harrowing that had taken place in the intervening period. This pesticide possibly represented previously buried residues which had been brought to the surface by the cultivation, and had then been released by subsequent rainfall. Isoproturon was also picked up occasionally below the surface in the suction samplers (0–4 μg litre^{-1}), nearly a year after its previous application. Clearly not all of the applied pesticide had been biodegraded within the expected timescale. This pesticide may have been protected in some way from degradation and only became mobile again during the very wet, late-winter period.

3.2 Pesticide persistence in the soil surface after spraying

Although the planned application of isoproturon on 12 March 1994 was 2·5 kg AI ha^{-1} ('Arelon'; Hoechst), an error on the part of the crop sprayer resulted in only 0·9 kg ha^{-1} (with a standard deviation, SD, of 0·23) being applied. The application rate was assessed by

analysis of the filter paper discs, and represented less than half the recommended application. Soil samples were also taken on day 0 from the top 2 cm of the soil, and revealed the presence of 5·4 mg kg^{-1} dry soil of isoproturon, with SD of 0·44.

The loss of isoproturon from the soil surface over time can be seen in Fig. 3. As observed in the previous season, the degradation of the compound initially proceeded rapidly, indicating a half-life of around 12 days. However, from day 40 to day 75 (21 April to 26 May) little or no degradation took place. This period coincided with dry weather and rapid crop growth. It would appear that the rainstorm of day 75 may have stimulated further degradation. In the previous season, the remaining soil-surface residues had also appeared to be more persistent from late April onwards.[6]

On day 121 (11 July) an attempt was made to assess whether pesticide residues had penetrated below the topsoil. From the soil pit 0·18 mg kg^{-1} was found in the top 2 cm, and 0·29 mg kg^{-1} between 2 and 10 cm. This indicates that in a heavy clay soil, pesticide cannot reach drain depth *via* movement through the matrix over the time course of a field season. Harris *et al.*[5] noted that, over 112 days, isoproturon was largely confined to the top 5 cm in a similar clay soil.

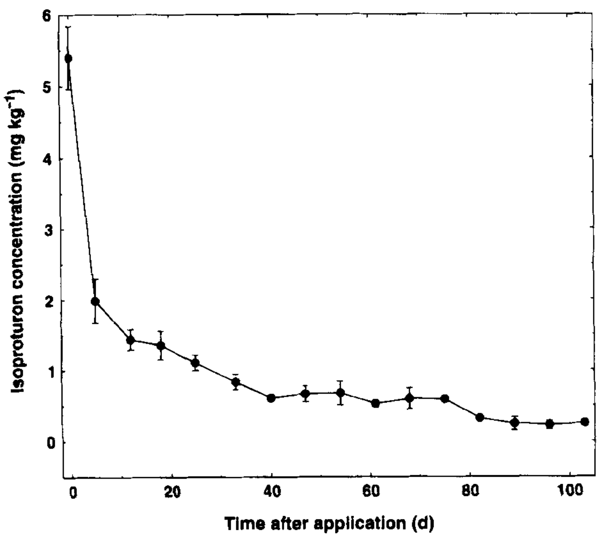

Fig. 3. Isoproturon present in the top 2 cm of soil at Wytham after application on 12 March 1994 (error bars represent the standard deviation from four replicates).

3.3 Isoproturon in rainwater

Isoproturon was detected in the collected rainwater before it had been applied to the local fields. From day 5 (17 Mar) and day 66 (17 May), isoproturon was regularly found in rainwater samples at concentrations ranging from 0·32 to 7·5 μg $litre^{-1}$ (Table 1). The highest concentration was found five days after the application of isoproturon to the field. It is not believed that pesticide entered the collectors *via* rain splash, as later work (unpublished) found that similar pesticide concentrations were present in collectors placed in a garden far from the field site. The pesticides may have arrived *via* dry or wet deposition.

3.4 Isoproturon and solute transport in rainfall events after application

From the application of isoproturon on 12 March 1994 until the end of the monitoring period in July, the rainfall was sufficient to generate bypass and drain flow on four separate occasions. These rain events totalled 56·5 mm, with 7·3 mm measured leaving the plot. This paper presents comprehensive monitoring data from the last two of these events.

3.4.1 *Pesticide transport on day 27 (8 April)*

Almost 25% of the 8·5 mm of rain which fell in the day 27 event was measured as leaving the plot (Table 2). The distribution of water and pesticide losses from the plot is shown in Fig. 4, with more pesticide being lost in the drain water than in the corresponding lateral subsurface water. Although the average concentrations of pesticide found on day 27 were half (maximum concentration of 130 μg $litre^{-1}$ in field drain water) that of an previous event eight days earlier, the overall loss of pesticide was larger as more water left the plot. Calculations on the loss of pesticides and solutes from the plot were as follows:

Isoproturon applied 0·9 kg ha^{-1} = 0·09 g m^2 = 54 g in a plot of 600 m^2 (described as initial isoproturon);
Soil samples taken from the top 2 cm of soil, where bulk density was 1·3 g cm^{-3};
1 m^2 × 0·02 m × 1300 = 26 kg, thus 1 m^2 to a depth of 2 cm which contains 26 kg soil;

TABLE 1
Isoproturon (μg $litre^{-1}$) Collected in Two Rainwater Samplers, Situated 20 m apart on the Field Site

Date	*22 Nov. 1993*	*17 Mar. 1994*	*30 Mar. 1994*	*8 April 1994*	*17 May 1994*
RW1	0·52[a]	7·5	1·14	0·32	0·13
RW2		6·4	2·14	0·59	0·04

[a] Both rainwater samples bulked together.

TABLE 2

Day 27 (8/4/94) Rainstorm (8·8 mm) and Day 75 (26/5/94) Rainstorm (16·5 mm) Event Data for Water Outflow and Isoproturon Transported from the Field Plot

Flow route	*Water Outflow (mm)*	*Outflow (%)*	*Proportion of rainfall (%)*	*Total isoproturon loss (mg)*	*Average isoproturon concentration (μg litre⁻¹)*	*Where loss distributed (%)*	*Loss of isoproturon present on the day (%)*	*Loss of initial isoproturon (%)*
Day 27								
Drain	1·34	65·7	15·7	92·6	115	76	0·53	0·170
Lateral-subsurface	0·64	31·5	7·5	27·7	72	22	0·16	0·050
Overland	0·06	2·8	0·6	3·6	105	3	0·02	0·006
Total	2·04	100·0	23·9	123·9		100	0·71	0·230
Day 75								
Drain	2·42	87	14·6	7·25	5	92·4	0·074	0·013
Lateral-subsurface	0·37	13	2·2	0·6	3	7·6	0·006	0·001
Overland	0	0	0·0	0·0	0	0	0·000	0·000
Total	2·79	100	16·8	7·85		100	0·08	0·014

Therefore, if 1·11 mg kg^{-1} isoproturon were present on day 25 this = 28·9 mg m^{-2}, or 17·3 g in 600 m^2 (isoproturon potentially available for transport from the soil surface).

The isoproturon potentially available for transport on the soil surface was based on the most recent measurement, with respect to the storm event, of the amount of isoproturon in the soil. Thus, to estimate how much pesticide has been lost due to an event, the volume of flow and the pesticide concentration at each time point can be used to calculate how much pesticide was lost for each 30 min. This was done for each outflow route to provide the data shown in Table 2.

The loss of isoproturon by all measured flow routes after this event amounted to 0·71% of that believed to be present in the soil surface at the time (Table 2). This corresponds to 0·23% of the isoproturon applied.

An additional calculation for isoproturon can be made using the K_d (equilibrium distribution coefficient) of 2·5 for isoproturon in Wytham soil. Assuming an equilibrium exists between the aqueous and sorbed phases of isoproturon then,

$$S = K_d . C \tag{1}$$

where S is the sorbed isoproturon concentration (μg kg^{-1} dry weight), and C is the aqueous concentration (μg litre^{-1}). The total pesticide present in any given depth of soil, T, is the total of the aqueous and sorbed phases,

$$T = SM + CV_w \tag{2}$$

where M is the mass of soil (kg, dry weight) and V_w is the volume of water. Substituting (1) into (2), rearranging and expressing the result in terms of soil volume, V_s gives:

$$C = T/V_s . \left(\frac{1}{K_d . \varrho + \Theta}\right) \tag{3}$$

where ϱ is the bulk density of the soil (kg litre^{-1}) and Θ (cm^3 cm^{-3}) is the soil water content. Thus, if the total pesticide content of a soil volume is known together with its bulk density, water content and its pesticide soil/water partition coefficient, the aqueous available pesticide concentration and amount can be calculated. This calculation was made for each of the pesticide run-off events, in order to estimate the total aqueous pesticide available that might be available to be leached from the soil.

Concentrations of isoproturon in soil were measured at various intervals following application. From these data the concentrations on the days of rainfall events were calculated by linear interpolation. These values represent the concentration in the top 2 cm of the soil and, for the purposes of the applications of the equations above, the majority of the pesticide was assumed to be in this top layer. The estimated maximum pesticide removal was calculated as 0·432 g; the observed figure was 28% of this value (Table 2). Thus, less isoproturon has been transported than might have been expected. Some explanations for this shortfall might include; the K_d figure was an underestimate, or pesticide was readsorbed to the soil during transit, or not all the aqueous-phase pesticide is actually available to the new rainwater.

The combined hydrograph and chemographs shown in Fig. 4 show a peaked, short duration, flow response of the drains to rainfall, which is characteristic of preferential water movement. Each sampling point on the

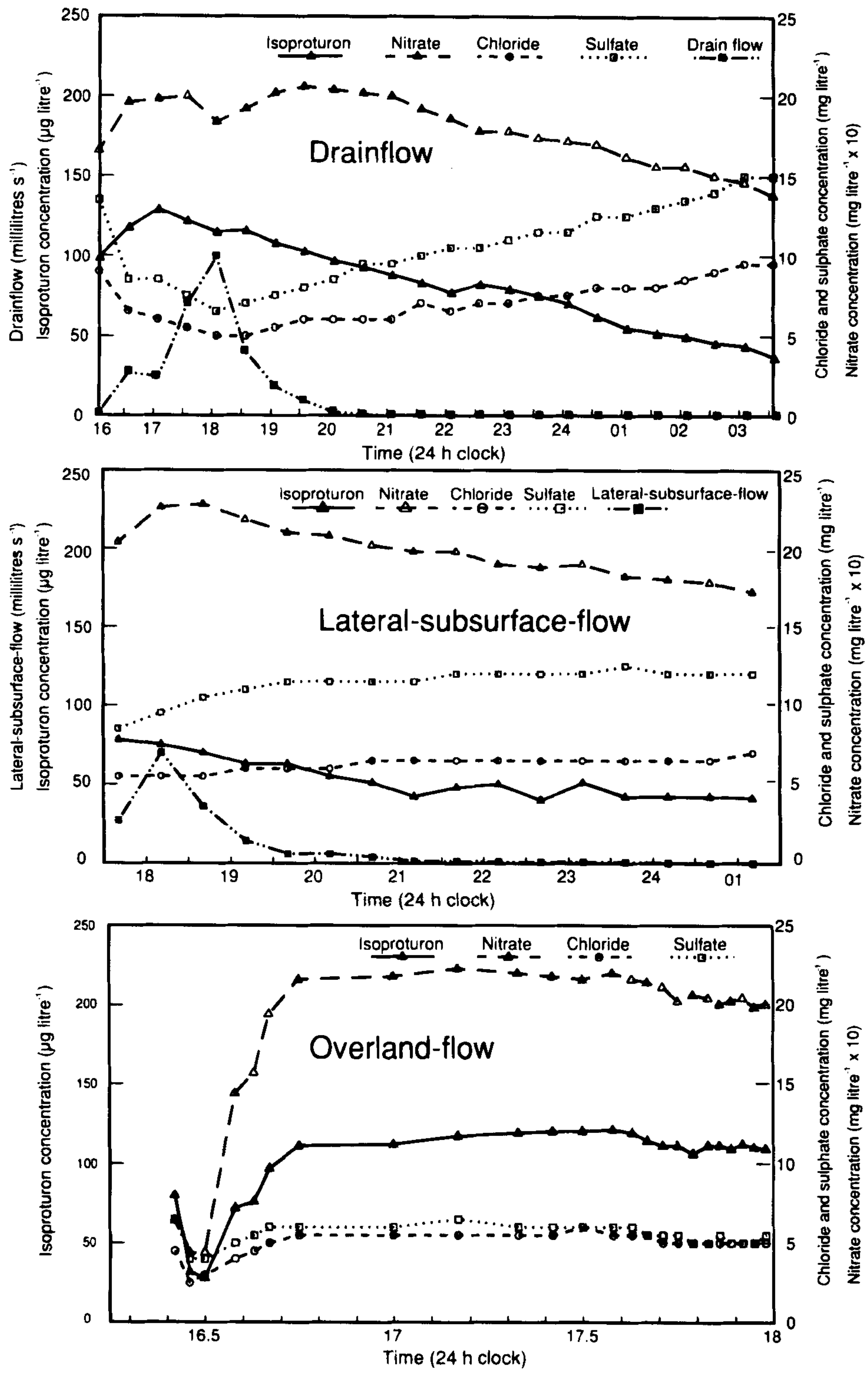

Fig. 4. Comparison of solute concentrations (isoproturon, nitrate, chloride and sulfate), analysed from water samples collected by autosampler with drain flow, lateral-subsurface flow and overland-flow for the rainfall event 27 days after isoproturon application.

overland-flow graph corresponds to the passage of 1 litre through the flow-measuring device. Over 90% of the water loss from the plot occurred over a period of not more than 4 h. The initiation of flow *via* these different preferential routes began at around 1600 h with lateral subsurface flow beginning 1 h later.

A relationship between drain-flow velocity, isoproturon and nitrate concentration can be observed in Fig. 4. It is believed that at maximum drain flow, the majority of the water has come directly from the soil surface, this being where the majority of both isoproturon and nitrate is located in the soil. Chloride and sulfate may

be located more evenly through the soil than isoproturon or nitrate. Suction samplers at 25 and 50 cm depth routinely yielded water with much higher chloride and sulfate concentrations than isoproturon or nitrate concentrations. Thus, the new rainwater has a low chloride and sulfate concentration with respect to the soil matrix as a whole (Table 3). The mixing of the new rainwater with the soil water will result in an increase in chloride and sulfate concentration for the new water; this re-equilibration will be dependent on the diffusion rate. Therefore, the more slowly the new water moves through the soil (for example at the beginning and at the end of the drainage period), the greater its chloride and sulfate concentration, and conversely the faster it moves through the soil the lower the salt concentration. Such a dilution in salt concentration in drain water has been observed before in connection with fast macropore flow.[14] This hypothesis may explain the inverse relationship between drain-flow velocity and chloride and sulfate concentrations.

The fluctuations in chloride and sulfate concentrations with water-flow velocity are not seen with lateral subsurface or overland flow (Fig. 4). Unlike the water which has reached the drains by vertical movement through 50 cm, the other lateral-flow pathways take place only in the upper few centimetres of the soil. However, the similarity in chloride and sulfate concentrations between drain water, lateral-subsurface water and overland-flow water, indicates a common origin for the preferential-flow water, although on this occasion the lateral-subsurface flow water appeared to have a higher salt concentration than that from the other flow paths. An unusual feature of the event, in terms of anion transport, was the very high nitrate concentrations (over 200 mg litre^{-1}), representing a loss of 4 kg ha^{-1} that had been transported out of the plot (Fig. 4). This may have been caused by the nitrification of urea fertiliser that was applied to the soil eight days previously (143 kg N ha^{-1}).

The overland-flow and drain-water isoproturon concentrations during the flow event were very similar (Fig. 4). Assuming that the drain water at the peak of the event was largely overland-flow water, no readsorption of pesticide was discernible. It is believed that all of the preferential-flow water was closely connected, yet the lateral-subsurface-flow water had much lower pesticide concentrations than either overland or drain water. As discussed earlier, the water may have moved laterally over an average distance of 15 m, through the organic-rich topsoil, to reach the collector of lateral-subsurface flow. In addition, the first sample of lateral subsurface flow was not collected until 1·5 h after the first drain samples because the low flow was insufficient to trigger the autosampler. It was therefore assumed that sorption was occurring to an extent not observed with the other preferential flow routes. The overland-flow water may also have travelled 30 m laterally to reach the collector. However, unlike the lateral-subsurface-flow water, it probably moved more quickly due to less resistance, coming into contact with less soil, and thereby reduced the readsorption potential.

3.4.2 Isoproturon and solute transport on day 75 (26 May)

By late May the crop was well established, and deep shrinkage cracks could be observed in the soil. Different patterns of hydrochemical behaviour were observed in the event on 26 May from that in April 48 days earlier. The rainfall on day 75 reached higher intensities than previously (up to 7 mm h^{-1}), and a greater volume of rain fell than on any previous occasion. The largest volume of water recorded as leaving the plot, 2·8 mm, occurred following this storm. However, notwithstanding the heavy rainfall, no overland flow was recorded and lateral subsurface flow was minimal (Table 2). A much higher proportion of outflow water was taken by the drainage system compared to the other flow routes than during the storms earlier in the year. It is probable that the shrinkage cracks intercepted overland water movement, allowing much of it to be channelled to the mole drains. Due largely to biodegradation, less pesticide was present in the soil prior to the rain storm than in previous events (1·11 mg kg^{-1} for day 25 and 0·6 mg kg^{-1} on day 75). In addition, it has been reported that the adsorption equilibria can change over time, and that a greater proportion of the pesticide becomes adsorbed with time.[15] The low pesticide concentrations of around 5 μg litre^{-1} noted in the drain water were

TABLE 3
Comparison of Chloride and Sulfate Concentrations (mg litre^{-1}) Emanating from the Field Drain during and at the End of the Day 27 Rainfall Event

Sample origin	*Drain at peak flow*	*Drain at end of flow*	*Overland flow*	*Lateral-subsurface flow*	*Rainwater*	*25 cm suction samplers*[a]
Chloride	5·0	10·0	5·0	6·5	1·5	11
Sulfate	7·0	15·0	5·0	11·0	2·5	37

[a] Average reading for suction samplers in March–April. Suction-sampler data represent the means of seven observations, SD for chloride 5·4, SD for sulfate 8·0.

therefore not unexpected (Fig. 5). The amount of pesticide lost with reference to that which was available on the day (0·6 mg kg^{-1}) was 0·08%, much lower than in the previous event (0·71%).

The calculation done for day 27 (to estimate total available isoproturon within the soil before the rainfall event) was repeated. In this case, the pesticide concentration in the top 2 cm was estimated as 0·59 μg $litre^{-1}$ and the water content was 0·47 (cm^3 cm^{-3}). This gave a total available mass of 1·2 g isoproturon at a concentration of 204 μg $litre^{-1}$. During the rainfall event, 0·073 g of isoproturon was measured leaving the plot (Table 2), 6·1% of that estimated to be in the aqueous phase. As with the day 27 event, less of the pesticide (21%) was transported than might have been estimated.

The pesticide concentration in lateral-subsurface-flow samples was again lower than that found in the drain water. The relationship between flow paths and chloride and sulfate concentrations was not as clear as on previous occasions. The background concentrations of chloride seen in the mole drain and suction sampler were similar to that found in rainwater (data not shown). It is difficult to explain the low chloride concentrations in the soil at this point in the season. At the very end of the drain flow, however, chloride and sulfate concentrations were higher than at peak drain flow, as had been observed on previous occasions.

3.5 Comparison of rainfall events on day 27 and 75

A greater proportion of the rainwater was absorbed by the soil on day 75 compared to day 27 (Fig. 6). No overland flow and very little lateral subsurface flow was recorded on day 75. The well-established crop and the deep shrinkage cracks in the field by day 75 would not have favoured lateral subsurface flow. This has also been observed in other moled clay soils.[5] The most significant difference observed between the two events, which were separated by 48 days, was the small amount of isoproturon transported on day 75 (only 6% of that transported on day 27). This can be related to the smaller quantity of pesticide left in the soil by this stage (0·6 compared to 1·11 mg kg^{-1}). As a smaller proportion of the potentially available pesticide was transported in the later event, it may be supposed that a greater proportion was more strongly bound, or less available for transport, at this time in the season. The potential of deep shrinkage cracks as important pollutant transport routes has been highlighted in studies of clay soils.[16,17] However, with an increasing soil water deficit in spring/summer, only a heavy storm might exceed the infiltration capacity of the soil matrix and thus initiate preferential flow.

3.6 The relative importance of different flow routes for water movement and pesticide transport

The total amounts of rainwater measured flowing out of the plot ranged from 8 to 24%. Of this, 63 to 87% left the plot in the drainage system. On the events when this occurred, no more than 3% of the outflowing water left the plot *via* overland flow. The quantity of outflow water in lateral-subsurface flow varied between 13 and 34%. The largest proportion of lateral-subsurface-flow

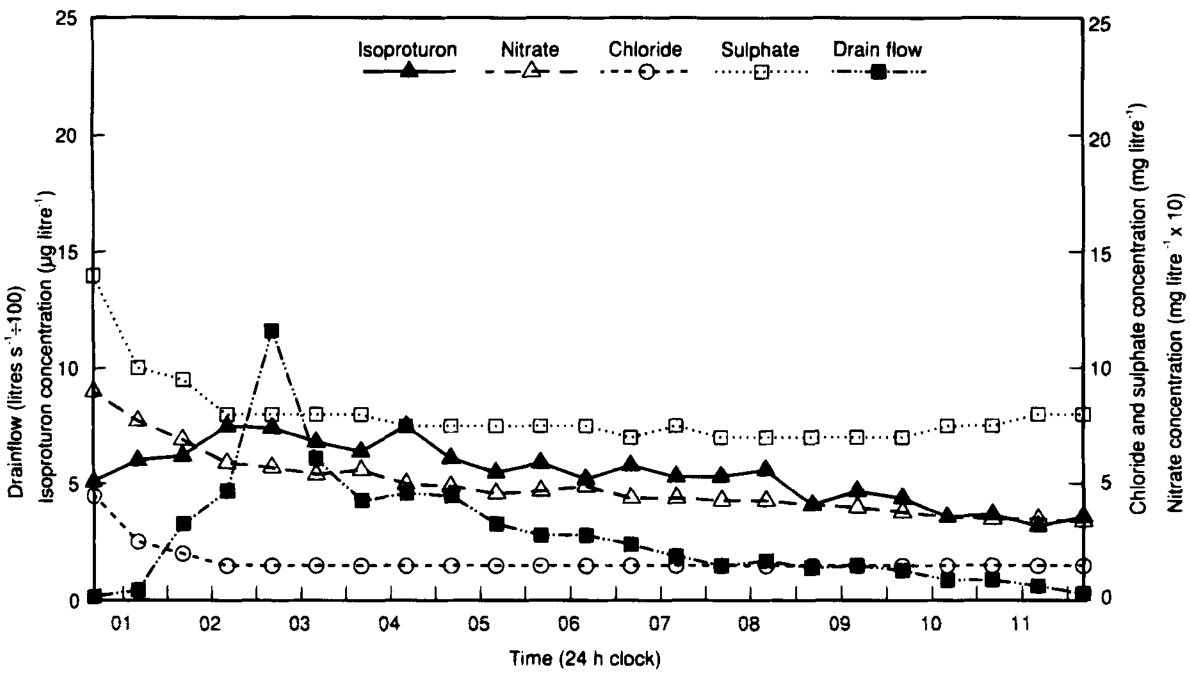

Fig. 5. Comparison of solute concentrations (isoproturon, nitrate, chloride and sulfate) analysed from water samples collected by autosampler with drain flow for the rainfall event 75 days after isoproturon application.

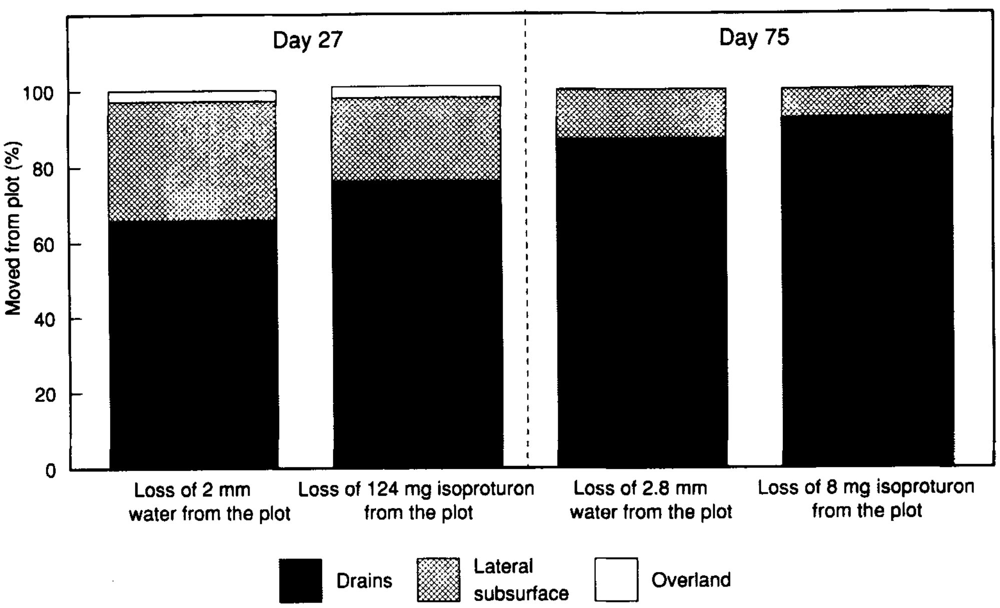

Fig. 6. Rainfall distribution and isoproturon loss from the plot from events on day 27 and 75.

water as a proportion of the whole was measured earlier in the season on 31 March 1994 (day 19),[18] and the smallest on 25 May 1994 (day 75). The dominance of drain flow over lateral-subsurface and overland flow in a mole-drained, clay loam soil was also reported by Brown *et al.*[7]

Although high pesticide concentrations could be found in overland-flow water, little of the rainwater left the plot by this route, and no more than 3% of the pesticide was lost from the plot in this manner. Notwithstanding the depth of the drains from the soil surface, the drain concentrations were very similar to those found in overland flow. This indicates that next to no pesticide was readsorbed as it moved down vertical macropores and within the drainage system. This is despite the organic matter coatings on worm burrows, which were described by Stehouwer *et al.*[19] as having a high sorption potential for pesticides. The use of a dye with undisturbed soil in mini-lysimeter experiments illustrated the important role of worm burrows in conveying water below 12 cm.[20] Due to the large volumes of water and high pesticide concentrations, the drainage system carried 75 to over 90% of the pesticide lost from the plot in the different rain events.

Of the three preferential-flow routes discussed, the lowest concentrations of pesticide were found in the lateral-subsurface-flow water. If all the preferential-flow water initially collects its pesticide from a pool at the soil surface before being transported in different directions, then the lateral-subsurface-flow water loses approximately one-third of its pesticide as it flows out of the plot. This is in contrast to other solutes, such as nitrate and chloride, in which the same proportions are carried as in the other flow routes (data not shown). This indicates that pesticide is being readsorbed as it travels through the soil *via* lateral-subsurface flow. In work done on lateral movement of isoproturon through soil at Cockle Park, Brown *et al.*[7] found no such trend in pesticide concentrations when comparing surface-layer flow with drain flow. However, at Cockle Park, surface-layer flow was a compilation of overland flow and subsurface flow, so a direct comparison cannot be made.

3.7 Comparison of pesticide behaviour and transport at Wytham in 1993 and 1994

In the 1993 season, pesticide degradation followed the expected pattern until late May.[6] From then on the small amount of residues left showed an increased persistence. Although the remaining pesticide appeared more persistent, it could still be mobilised in rain events. Similarly, in 1994 from late April onwards the pesticide appeared to be more persistent. Analysis of the weather and soil hydrological data for 1994 showed a developing soil moisture deficit in the topsoil during this period. This would reduce microbial activity because of moisture stress, and so reduce degradation.[21]

As in the 1993 season, the pesticide was applied in late winter/early spring in 1994 and rain events leading to drain flow occurred in March and April. A maximum concentration of 500 μg litre^{-1} was noted in the drain water on 1 April 1993 and 290 μg litre^{-1} on 31 March 1994.[18] However, for the 1993 event, more pesticide was present in the soil (2·9 mg kg^{-1}) than for the 1994 event (1·4 mg kg^{-1}). A greater amount of water (and thus loss of pesticide) through the drains was measured in the 1993 events. The estimated cumulative loss of applied pesticide to the drainage system for the 1992/93 season was 1·5%.[6] No more than 16% of rainfall left the plot *via* the drains in the 1994 season. More rainwater

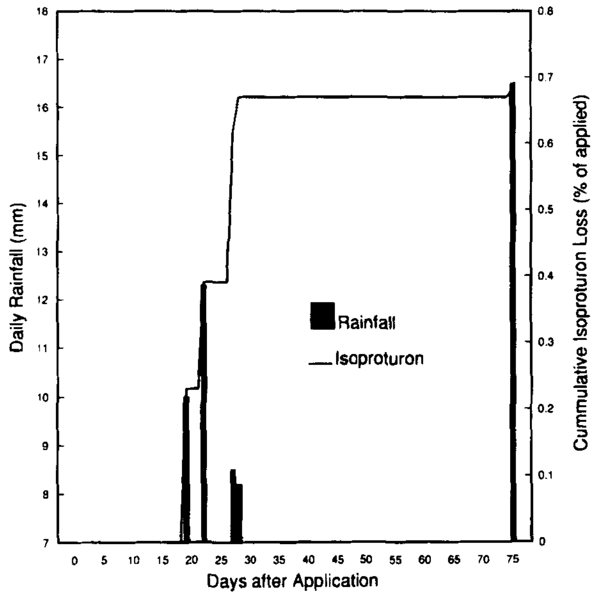

Fig. 7. Daily rainfall and cumulative isoproturon loss for the 1993–94 season.

appeared to be held by the soil in 1994. This can probably be attributed to the mole drain network decaying since the previous season, when it had only recently been created. An assessment of the activity of the mole drains which crossed the plot was also made in 1994.[21] Water flowed through only 50% of the mole drains in response to rainfall, and the volumes carried varied by up to an order of magnitude between the working moles. The cumulative loss of the applied pesticide (0·7%) for the 1993/94 season is shown in Fig. 7.

4 CONCLUSIONS

Isoproturon residues could be found in soil water from the previous year's application. This indicated that a small proportion had persisted in the topsoil almost a year after its application. Although pesticide concentrations were high, overland flow as a mechanism for pesticide transport was insignificant in this field due to the efficiency of the drainage system. Lateral subsurface flow was more important than overland flow, but less important than drain flow in terms of the load of pesticide carried. It may be that pesticide transported for long distances laterally within the topsoil was more subject to readsorption than the other flow routes.

The heavy rainfall event in late May did not result in high pesticide loss, despite the presence of extensive shrinkage cracks. Most of the pesticide had been degraded by this stage, so little was available for transport. Vertical macropores play a major part in conveying water to the drainage system. The similarity in isoproturon concentrations between overland flow and drain flow suggested that the vertical macropores, including worm burrows, did not adsorb significant quantities of pesticide. Over the course of the field season, notwithstanding variations in rainfall intensity, calculations based on measurements of volume and antecedent soil conditions suggested that less of the aqueous phase of the pesticide was transported in storm events over the season. This may indicate a change in adsorption equilibrium over time.

The pesticide concentrations found in runoff water from the Wytham field site are among the highest reported in European literature. These high concentrations can be ascribed to (a) the relative mobility of the compound; (b) the rapidity of water movement through the soil, minimising the opportunities for pesticide readsorption; (c) the fact that there is no interaction of storm water with a deeper water table, where dilution might take place and (d) the efficiency of the drainage network in collecting new storm water.

Even with farmers following good agricultural practice on a drained clay soil, herbicides applied to winter cereals will reach nearby streams and ditches at levels which could give rise to concern. Water companies have now highlighted the agricultural use of isoproturon as a major factor in non-compliance with the EC water quality targets.[4] The current design of uncultivated buffer strips, such as the one at the bottom of our fieldsite, can prevent direct overspraying of water courses and prevent overland flow from directly entering streams and ditches. However, our research has highlighted the role of the drainage system in transporting pesticide to the nearby stream. As the drains run under the buffer zone, such a zone cannot affect this major contamination route.

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REFERENCES

1. Harris, G. L., Goss, M. J., Dowdell, R. J., Howse, K. R. & Morgan, P., A study of mole drainage with simplified cultivation for autumn-sown crops on a clay soil. 2. Soil water regimes, water balances and nutrient loss in drain water 1978–1980. *J. Agric. Sci. Cam.*, **102** (1984) 561–81.
2. Williams, R. J., Brook, D. N., Glendinning, P. J., Matthiessen, P., Mills, M. J. & Turnbull, A., Movement and modelling of pesticide residues at Rosemaund farm. *Proc. 1991 Brighton Crop Prot. Conf.—Weeds*, **2** pp. 507–14.

3. Traub-Eberhard, U., Henschel, K., Kördel, W. & Klein, W., Influence of different field sites on pesticide movement into subsurface drains. *Pestic. Sci.*, **43** (1995) 121–9.
4. White, S. L. & Pinkstone, D. C., The occurrence of pesticides in drinking water. *British Crop Protection Council Monograph No 62: Pesticide movement to water*, BCPC, Farnham, Surrey, UK, 1995, pp. 263–8.
5. Harris, G. L., Nicholls, P. H., Bailey, S. W., Howse, K. R. & Mason, D. J., Factors influencing the loss of pesticides in drainage from a cracking clay soil. *J. Hydrol.*, **159** (1994) 235–53.
6. Johnson, A. C., Haria, A. H., Bhardwaj, C. L., Völkner, C., Batchelor, C. H. & Walker, A., Water movement and isoproturon behaviour in a drained heavy clay soil: 2. Persistence and transport. *J. Hydrol.*, **163** (1994) 217–31.
7. Brown, C. D., Hodgkinson, R. A., Rose, D. A., Syers, J. K. & Wilcockson, S. J., Movement of pesticides to surface waters from a heavy clay soil. *Pestic. Sci.*, **43** (1995) 131–40.
8. Williams, R. J., Brooke, D. N., Matthiessen, P., Mills, M., Turnbull, A. & Harrison, R. M., Pesticide transport to surface waters within an agricultural catchment. *J. Inst. Wat. Environ. Man.*, **9** (1995) 72–81.
9. Rönnefahrt, I., Fliedner, A., Remde, A., Traub-Eberhard, U. & Rebus, D., Aquatic microcosms as a tool for assessing fate and effects of pesticides. *Brighton Crop Prot. Con.—Pests and Diseases 1994*, 1355–60.
10. Matthiessen, P., Sheahan, D., Harrison, R., Kirby, M., Ryecroft, R., Turnbull, A., Volkner, C. & Williams, R. J., Use of *Gammarus pulex* bioassay to measure the effects of transient carbofuran runoff from farmland. *Ecotox. Environ. Safety*, **30** (1995) 111–19.
11. Jarvis, M. G. & Hazelden, J., Soils in Oxfordshire 1, Soil Survey Record No. 77. *Soil Survey of England and Wales*, Rothamsted Experimental Station, Harpenden, 1982, pp. 53–64.
12. Trafford, B. D., Improving the design of practical field drainage. *Soil Sci.*, **118** (1975) 334–8.
13. Haria, A. H., Johnson, A. C., Bell, J. P. & Batchelor, C. H., Water movement and isoproturon behaviour in a drained heavy clay soil: 1. Preferential flow processes. *J. Hydrol.*, **163** (1994) 203–16.
14. Andreu, L., Moreno, F., Jarvis, N. J. & Vachaud, G., Application of the model MACRO to water movement and salt leaching in drained and irrigated marsh soils, Marismas, Spain. *Agric. Water Man.*, **25** (1994) 71–88.
15. Walker, A., Welch, S. J. & Turner, I. J., Studies of time-dependent sorption processes in soils. *British Crop Protection Council Monograph No 62: Pesticide movement to water*, BCPC, Farnham, Surrey, UK, 1995, pp. 13–18.
16. White, R. E., Dyson, J. S., Gerstl, Z. & Yaron, B., Leaching of herbicides through undisturbed cores of a structured clay soil. *Soil Sci. Soc. Am. J.*, **50** (1986) 277–83.
17. Bronswijk, J. J. B., Hamminga, W. & Oostindie, K., Field-scale solute transport in a heavy clay soil. *Wat. Resour. Res.*, **31** (1995) 517–26.
18. Johnson, A. C., Haria, A. H., Cruxton, V. L., Batchelor, C. H. & Williams, R. J., Isoproturon and anion transport by preferential flow through a drained clay soil. *British Crop Protection Council Monograph No 62: Pesticide movement to water*, BCPC, Farnham, Surrey, UK, 1995, pp. 105–10.
19. Stehouwer, R. C., Dick, W. A. & Traina, S. J., Sorption and retention of herbicides in vertically orientated earthworm and artificial burrows. *J. Environ. Qual.*, **23** (1994) 286–92.
20. Johnson, A. C., The use of mini-lysimeters to study the influence of rainfall intensity on pesticide transport and water pathways. *British Crop Protection Council Monograph No 62: Pesticide movement to water*, BCPC, Farnham, Surrey, UK, 1995, pp. 33–8.
21. Walker, A., Review: Influence of soil and weather factors on the persistence of soil applied herbicides. *App. Plant Sci.*, **5** (1991) 94–8.
22. Johnson, A. C., Batchelor, C. H. & Haria, A. H., Processes influencing pesticide transport in a drained clay catchment. *Effects of Scale on Interpretation and Management of Sediment and Water Quality (Proceedings of the Boulder Symposium, July 1995)*. IAHS Publ. no. 226, 1995, pp. 39–46.